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Optical properties of GaN nanostructures for optoelectronic applications

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Abstract

Electrochemical deposition method is used to prepare GaN nanostructure. The morphological studies using scanning electron microscopy (SEM), photoluminescence (PL) the refractive index and optical dielectric constant are investigated experimentally and theoretically, respectively. These investigations are found to be dependent on the growth time. The nanosize effect is noticed for UV detectors applications. The calculated results are in agreement with experimental and theoretical data.

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1. Introduction

Gallium nitride has a wide and direct wide band gap semiconductor (3.39 eV) at room temperature, in addition, operating at blue and ultraviolet wavelengths at high temperature [1]. Within last two decades, distinguished efforts have been put to study GaN theoretically [2-5] and to grow GaN thin films by metalorganic chemical vapour deposition (MOCVD) [6], reactive molecular beam epitaxy (MBE) [7], hydride vapour phase epitaxy (HVPE) [8] and reactive sputtering [9], experimentally. However to avoid expensive techniques of very high cost, it is resumed to search for effective-cost technique, namely electrochemical deposition (ECD).

The growth mechanism of GaN nanostructure by ECD as a function of deposition time is attractive. In this work, the synthesis of GaN nanostructure using with a simple one-step ECD on n-Si (1 1 1) substrates for different durations and the effects of deposition duration on the quality and on the properties of GaN nanostructure are reported. Structural, morphological and optical properties are investigated by scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy.

2. Experimental Procedure

GaN nanostructures were prepared by electrochemical technique in one step using an aqueous solution consisting of a mixture of gallium nitrate ($Ga(NO_3)_3$) with ammonium nitrate (NH_4NO_3) in the ratio of (1:1) in deionized water kept at atmospheric pressure, and at 20 ^oC since Ga metals melts at 29 ^oC [10,11]. The substrate of n-type Si (1 1 1) was used.

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Before deposition, Si (1 1 1) was cut into 1 cm x 1 cm substrates, the substrates were cleaned with 50:10:10 $H_2O/NH_4OH/H_2O_2$ for 10 min firstly, with 1:50 $HF:H_2O$ for 10 min secondly and thirdly with 60:10:10 $H_2O/HCl/H_2O_2$ at 80 ^oC for 10 min to remove the surface oxides. Between the cleaning steps, the substrates were rinsed in deionized water. A simple homemade Teflon cell with two electrodes was used. A gallium plate with 99.999% purity was used as an anode and n-Si (1 1 1) as a cathode.

The distance between anode and cathode was about 0.5 cm [12]. In the electrochemical deposition process, it was used constant current density J = 2.5 mA/cm^2 (supplied by a Keithley 220 programmable current source) for different duration times: t = 6, 12, 24 and 48 h. The deposited films underwent a series of material characterization techniques, namely scanning electron microscopy (SEM), X-ray diffraction (XRD) and photoluminescence (PL) spectroscopy performed at room temperature. Finally, the nanostructure thickness was measured using an optical reflectometer (Filmetrics F20).

3. Results and Discussion

3.1. Morphology of GaN nanostructures

It is shown that the scanning electron microscopy images of GaN nanostructure deposited on Si (1 1 1) substrates using ECD are in Fig. 1. The deposition is done for different durations: 6, 12, 24 and 48 h, keeping the current density 2.5 mA/cm^2 (corresponding to the applied potential voltage of 15 V) constant. The SEM images show different surface morphologies of the grown structures on Si substrate according to the deposition durations. For the 6 h duration (Fig. 1(a)), GaN nanostructure started depositing with some spaces on the Si substrates and with thickness about 100 nm. For the 12 h duration (Fig. 1(b)), network of nanoflakes was formed. The flakes were a mixture of large and small sizes from a micron to 100 nm with film thickness of about 180 nm. While, for the deposition of 24 h duration (Fig. 1(c)), the nanoflakes became compact with three- dimensional sponge-like structures and the thickness is increased to 260 nm. Lastly, for the longest duration of 48 h (Fig. 1(d)), the nanostructure became uniform, compact, crystallized, symmetry cell- like and the thickness increased to 270 nm. It is noticed that the deposition duration has a significant effect on the morphology, the shape, the thickness and the size of the structures, the dimensions of the structures increase as deposition time increases.

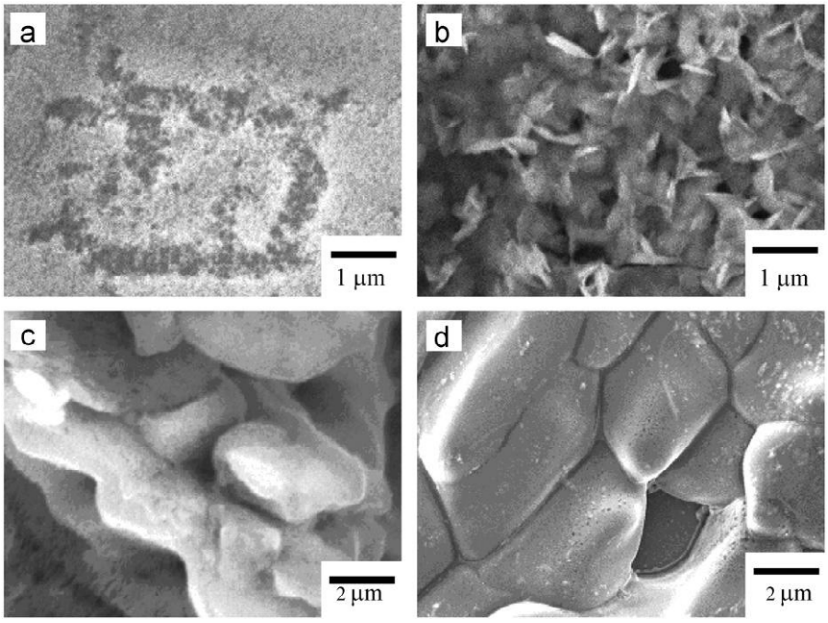

Fig. 1. Scanning electron microscopy images of the four GaN nanostructures deposited of different durations for (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 [12]

3.2. Optical properties of GaN nanostructures

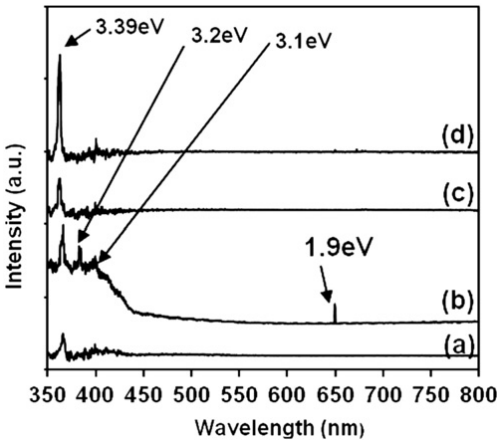

Fig. 2. PL spectra of the four GaN nanostructures deposited of different durations for (a) 6 h, (b) 12 h, (c) 24 h and (d) 48 h [12]

The photoluminescence (PL) spectra of GaN nanostructure on Si substrate for different deposition times is shown in Fig. 2, revealing four peaks at 3.39, 3.2, 3.1 and 1.9 eV. The peak positions at 3.39 and 3.2 eV are due to the band gap of h-GaN and c-GaN, respectively, and these values are in accordance with other theoretical and experimental results [13,14] as shown in Table 1. The first peak at 3.39 eV is observed on the four structures and its intensity increases as the deposition time increases. The second peak 3.2 eV is observed on all structures, indicating that c-GaN existed on all samples and it is more observable on the deposition for 12 h (Fig. 2b). The third peak centered at 3.1 eV observed on all structures with low intensity and it may be due to the donor acceptor (DA) transition [20]. The last peak at 1.9 eV has low intensity and it is noticed only on deposition for 12 h (Fig. 4b), which may be due to the deep level states related to gallium or nitrogen vacancy [21].

Table 1. Energy gap (ev), refractive index using Ravindra et al. [15], Herve and Vandamme [16], Ghosh et al. [17] models and optical dielectric constant determined for nanostructure gan deposited for different times.

Time (h)	E_g *(eV)*	n	ε_∞
6	-	-	-
12	1.9	2.87[c] 2.75[d] 2.85[e]	8.237[c] 7.562[d] 8.122[e]
24	3.2	2.064[c] 2.29[d] 2.282[e]	4.260[c] 5.244[d] 5.207[e]
48	3.39 3.50[a] 3.50[b]	1.94[c] 2.238[d] 2.224[e] 2.399[#]	3.763[c] 5.008[d] 4.946[e] 8.9[$]

a: Ref. [13] Theo.; b: Ref. [14] Exp.; c: Ref. [15]; d: Ref. [16]; e: Ref. [17]; #: Ref. [18] Exp.; $: Ref. [19] Exp.

The refractive index n is a very important physical parameter related to the microscopic atomic interactions. From theoretical view point, there are basically two different approaches of viewing this subject: the refractive index will be related to the density and the local polarizability of these entities [22]. Consequently, many attempts have been made in order to relate the refractive index and the energy gap E_g through simple relationships [15,23-27]. However, these relations of n are independent of temperature and incident photon energy. Here the various relations between n and E_g will be reviewed. Ravindra et al. [15] had presented a linear form of n as a function of E_g:

$$n = \alpha + \beta E_g \tag{1}$$

where $\alpha = 4.048$ and $\beta = -0.62$ eV-1. Light refraction and dispersion will be inspired. Herve and Vandamme [16] have proposed an empirical relation as follows:

$$n = \sqrt{1 + \left(\frac{A}{E_g + B} \right)^2} \tag{2}$$

where $A = 13.6$ eV and $B = 3.4$ eV. For group-IV semiconductors, Ghosh et al. [17] had published an empirical relationship based on the band structure and quantum dielectric considerations of Penn [28] and Van Vechten [29]:

$$n^2 - 1 = \frac{A}{(E_g + B)^2} \tag{3}$$

where $A = 8.2E_g + 134$
$B = 0.225E_g + 2.25$ and ($E_g + B$) refers to an appropriate average energy gap of the material. Thus, using these three models the variation of *n* with energy gap has been calculated. The calculated refractive indices of the end-point compounds are listed in Table 1. This is verified by the calculation of the optical dielectric constant ε_∞ which depends on the refractive index. Note that $\varepsilon_\infty = n^2$ [30]. It is cleared that the calculated n using the model of Herve and Vandamme is in accordance with the experimental data [18,19] due to reflectivity parameter is important in enhancing the UV detector applications. This gives a recommendation for high detector efficiency at high absorption and low reflection spectrum.

4. Conclusion

The electrochemical deposition (ECD) is a suitable technique to demonstrate the synthesis of GaN nanostructure for different durations. The effects of deposition time on the quality of GaN nanostructure are investigated. SEM images indicated that the deposition duration has a significant effect on the morphology, the shape and the size of GaN structures, where the dimensions of the structures increase as the deposition durations increase. It is confirmed that PL spectra has the presence of mixed phases of h-GaN and c-GaN. From PL spectrum, it is indicated that the h-GaN band gap intensity increases as the deposition time increases. It is stated about possibility to use the effective-cost technique to grow GaN nanostructure on Si substrate suitable for photodetection. Finally, Herve and Vandamme have proved that it is more appropriate model for UV detectors applications.

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